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SCATTERING OF ATOMS BY SOLID SURFACES. I

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A quantum mechanical theory of the scattering of atoms by solid surfaces is presented. The theory is applied to a detailed discussion of elastic scattering (diffraction) processes, and the extension to inelastic scattering (phonon exchange) processes is discussed briefly. A great advantage of the theory is that scattering intensities of any size are easily handled; the moduli of the scattering matrix elements are not restricted to be small. If the results are expanded to lowest order in these moduli, then the "first order distorted wave Born approximation" is recovered. An example of the results obtained is that the intensity of the specularly scattered beam is by no means always larger than other diffracted intensities; this result is in agreement with experiments, and is a decided improvement over the usual first order treatments.

1. Introduction

The scattering of atoms by solid surfaces is by no means well understood, either experimentally or theoretically. If a sufficiently high level of understanding of this scattering could be reached, there is no doubt that atom–surface scattering could form a very useful tool indeed for studies of the properties of the single surface atomic layer of a solid. This is because, under normal conditions, incident atoms do not penetrate substantially beyond the first surface layer of a solid. These remarks are particularly true in view of the advent of controllable nearly-monoenergetic atomic beams[1–4]). As an example, such studies could be used to investigate surface phonon spectra of solids[5]). Low energy electron diffraction, while an exceedingly useful tool in its own right, does not yield much information concerning the *single* surface layer, because even electrons of quite low energy penetrate many solid surface layers.

For experiments of this nature to be useful, it is essential that a sufficiently good theory be available to interpret the results. It is clear that the *basis* of any complete theory of atom–surface scattering must be a quantum mechanical theory of inelastic scattering. However, the classical mechanical

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theory[6–9]) is in a considerably better state than is the quantum theory[10,11]). This situation is understandable because the classical theory can deal relatively easily, and perhaps correctly, with those large atom–surface energy and momentum transfers which are relevant to much recent research; examples are the drag forces on artificial earth-satellites and the efficiency of cryopumps. In quantum language, these transfers are results of "many-phonon" processes, which are not at all well understood. However, even one-phonon processes have not been adequately dealt with, although some theoretical progress has been made[10,11]). Perhaps the most remarkable statement which can be made in this context is that even *zero*-phonon processes (that is completely elastic diffraction processes) do not yet have an adequate theoretical interpretation.

Conventional quantum atom–surface elastic scattering theory, as used, for example, by Lennard-Jones and his coworkers[12]), is based on a first order distorted wave Born approximation. That this approach is inadequate for a useful description of experimental elastic scattering data is shown by the following remarks. This first order approximation is not valid if the total non-specular flux is large; that is, it is valid only if the specular beam contains considerably more flux than do all the other beams together. However, recent experimental data, for example those of Fisher and his coworkers[4]), show that the specular beam does not always contain the largest flux. Indeed, at least for not too glancing an incidence, the specular flux is usually *less* than the flux of even a *single* diffracted beam; in fact, the specular beam occasionally seems to vanish completely, even though first-order diffracted beams are at the same time readily visible.

The authors' view is that, before an adequate quantum theory of *inelastic* atom–surface scattering can be developed, an adequate *elastic* theory must be developed. Then, hopefully, many-phonon processes may be incorporated into the theory in a natural manner, starting perhaps with one-phonon processes. Eventually, it is hoped that the results of the classical theory may be obtained, by means of a limiting procedure, from the many-phonon quantum theory. The object of this paper is to present a new theory of elastic scattering which, it is hoped, will form the basis for the future work described above. The extension to inelastic scattering is discussed briefly.

2. Development of notation

The instantaneous potential energy of interaction of an atom (called the "gas atom") with a solid is denoted by $V(\boldsymbol{r}, \boldsymbol{u})$ where $\boldsymbol{r}$ is the position of the gas atom and $\boldsymbol{u}$ represents the displacements of all the solid atoms. The value of $V(\boldsymbol{r}, \boldsymbol{u})$ averaged over the thermal motions of the solid atoms is

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denoted by $v(\boldsymbol{r})$, which is called the "thermally-averaged potential energy function"; this is written as follows:

$$v(\boldsymbol{r}) = \langle V(\boldsymbol{r}, \boldsymbol{u})\rangle . \tag{2.1}$$

It is the function $v(\boldsymbol{r})$ rather than $V(\boldsymbol{r}, \boldsymbol{u})$ which is important in our elastic scattering theory; $V(\boldsymbol{r}, \boldsymbol{u})$ becomes important in the inelastic scattering theory (see, for example, section 7).

Where $\boldsymbol{k}$ is the incident wave-vector, M is the mass, and $\Psi(\boldsymbol{r})$ is the wave-function of the gas atom, the Schrödinger equation is

$$(\nabla^2 + k^2 - 2Mv(\boldsymbol{r})/\hbar^2)\, \Psi(\boldsymbol{r}) = 0 . \tag{2.2}$$

The z-direction is chosen as the outward normal to the surface, and $\boldsymbol{R}$ is defined as the two-dimensional position-vector (x, y) of the gas atom parallel to the surface; that is,

$$\boldsymbol{r} = (x, y, z) = (\boldsymbol{R}, z) . \tag{2.3}$$

The solid surface is assumed perfect in the usual sense; that is, the surface atoms are assumed to form a perfect, two-dimensional, infinite, periodic array. Incident atoms are assumed unable to penetrate beyond this surface layer under normal conditions. These assumptions result in a two-dimensional reciprocal lattice, each vector of which is parallel to the surface; the reciprocal lattice vectors are denoted by $\boldsymbol{G}, \boldsymbol{G}'$.

We define

$$v_{\boldsymbol{G}}(z) = L^{-2} \int\limits_{\text{surface}} v(\boldsymbol{r})\, \mathrm{e}^{-\mathrm{i}\boldsymbol{G}\cdot\boldsymbol{R}}\, \mathrm{d}^2\boldsymbol{R} , \tag{2.4}$$

where L^2 = surface area; the inverse of (2.4) is

$$v(\boldsymbol{r}) = \sum_{\boldsymbol{G}} v_{\boldsymbol{G}}(z)\, \mathrm{e}^{\mathrm{i}\boldsymbol{G}\cdot\boldsymbol{R}} . \tag{2.5}$$

The convention is introduced that sums over reciprocal lattice vectors $\boldsymbol{G}$ are over all $\boldsymbol{G}$, including $\boldsymbol{G}=0$, unless otherwise indicated. The wave-function $\Psi(\boldsymbol{r})$ may be expanded as follows:

$$\Psi(\boldsymbol{r}) = \sum_{\boldsymbol{G}} \Psi_{\boldsymbol{G}}(z)\, \mathrm{e}^{\mathrm{i}(\boldsymbol{K}+\boldsymbol{G})\cdot\boldsymbol{R}} , \tag{2.6}$$

where $\boldsymbol{K}$ is the component (k_x, k_y) of $\boldsymbol{k}$ parallel to the surface:

$$\boldsymbol{k} = (k_x, k_y, k_z) = (\boldsymbol{K}, k_z) . \tag{2.7}$$

For future reference, we note that

$$k_z^2 = k^2 - K^2 . \tag{2.8}$$

It is observed from the above definitions that a three-dimensional vector is denoted by a lower case letter, for example $\boldsymbol{k}$. The corresponding two-dimensional vector, parallel to the surface, is denoted by the corresponding capital letter, for example $\boldsymbol{K}$; the z-component, perpendicular to the surface, is denoted by a subscript z, for example k_z. This notation is made explicit in (2.7). The only exception to this notation is the vector $\boldsymbol{r}$, the z-component of which is denoted simply by z; see (2.3). A reciprocal lattice vector, for example $\boldsymbol{G}$, has no three-dimensional counterpart in this theory.

Substitution of (2.5) and (2.6) into (2.2) gives

$$\sum_{\boldsymbol{G}} \left(\frac{d^2 \Psi_{\boldsymbol{G}}}{dz^2} + k_{\boldsymbol{G}z}^2 \Psi_{\boldsymbol{G}} - \frac{2M}{\hbar^2} \sum_{\boldsymbol{G}'} v_{\boldsymbol{G}-\boldsymbol{G}'} \Psi_{\boldsymbol{G}'} \right) e^{i\boldsymbol{G}\cdot\boldsymbol{R}} = 0, \tag{2.9}$$

where $k_{\boldsymbol{G}z}$ is defined by analogy with (2.8):

$$k_{\boldsymbol{G}z}^2 = k^2 - (\boldsymbol{K} + \boldsymbol{G})^2. \tag{2.10}$$

Thus we note from (2.8) and (2.10) that k_z and $k_{\boldsymbol{0}z}$ are identical.

Each term of the outer summation in (2.9) vanishes separately:

$$\left(\frac{d^2}{dz^2} + k_{\boldsymbol{G}z}^2 - \frac{2M}{\hbar^2} v_0 \right) \Psi_{\boldsymbol{G}} = \frac{2M}{\hbar^2} \sum_{\boldsymbol{G}' \neq \boldsymbol{G}} v_{\boldsymbol{G}-\boldsymbol{G}'} \Psi_{\boldsymbol{G}'}. \tag{2.11}$$

The interpretation of $v_0(z)$ follows from (2.4) with $\boldsymbol{G}=\boldsymbol{0}$; that is, $v_0(z)$ is the thermally-averaged potential energy function, $v(\boldsymbol{r})$, averaged over the directions x and y parallel to the surface .The potential $v_0(z)$ is associated with a complete set, $\phi_\alpha(z)$, of eigenstates. Greek subscripts α, β stand for both states of negative energy and states of positive energy; negative-energy states are denoted by subscripts m, n and positive-energy states by subscript q. The Schrödinger equation defining the $\phi_\alpha(z)$ is

$$\left(\frac{d^2}{dz^2} + \alpha^2 - \frac{2M}{\hbar^2} v_0(z) \right) \phi_\alpha(z) = 0, \tag{2.12}$$

where

$$\alpha^2 \equiv q^2 \quad \text{if} \quad \alpha = q, \tag{2.13a}$$

and

$$\alpha^2 \equiv -k_n^2 \quad \text{if} \quad \alpha = n. \tag{2.13b}$$

With these definitions, the eigenvalue, E_α, of the energy of the state α is

$$E_\alpha = \hbar^2\alpha^2/2M, \tag{2.14}$$

for both negative-energy states ($E_n \leqslant 0$) and positive-energy states ($E_q \geqslant 0$). Normalization of any state is by means of "box normalization", the cubic

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box having side L, where $L\to\infty$:

$$\lim_{L\to\infty}\int_{-\frac{1}{2}L}^{+\frac{1}{2}L} |\phi_\alpha(z)|^2\,\mathrm{d}z = 1\,. \tag{2.15}$$

Hence, the positive-energy states may be called "continuum states", and the negative-energy states "bound states". The number of bound states is denoted by B.

It is convenient to choose the ϕ_α to be real. For q sufficiently small, the potential $v_0(z)$ gives rise to total reflection and the asymptotic forms of the $\phi_\alpha(|z|\to\infty)$ are:

$$\phi_n(|z|\to\infty) = 0,\qquad \phi_q(z\to-\infty) = 0\,, \tag{2.16a}$$

and

$$\phi_q(z\to\infty) = 2L^{-\frac{1}{2}}\cos(qz+\xi_q)\,, \tag{2.16b}$$

where ξ_q is a (non-arbitrary) phase.

The energy of a bound state is E_n, but the *total* energy of an atom in the state is larger than E_n by an amount equal to the kinetic energy associated with its motion parallel to the surface. This total energy is denoted by E_{nG}, where

$$E_{nG} = E_n + \hbar^2(\boldsymbol{K}+\boldsymbol{G})^2/2M\,. \tag{2.17}$$

This energy need not be equal to the incident energy, denoted by E:

$$E = \hbar^2 k^2/2M\,, \tag{2.18}$$

of the atom because the atom is in the bound state only temporarily. On the other hand, the total energy of the atom in a final diffracted state *is* equal to E. The term "diffracted state" is understood to include the specular state.

The following addition to the notation is made: reciprocal lattice vectors associated with final diffracted states may be denoted by $\boldsymbol{F}, \boldsymbol{F}'$; that is, $\boldsymbol{G}, \boldsymbol{G}'$ stand for *any* reciprocal lattice vectors, whereas $\boldsymbol{F}, \boldsymbol{F}'$ stand *only* for those linking the initial state to final diffracted states. The zero reciprocal lattice vector, which links the initial state to the specular state, is included as one of the $\boldsymbol{F}$. As with $\boldsymbol{G}$, sums over $\boldsymbol{F}$ are over all $\boldsymbol{F}$, including $\boldsymbol{F}=\boldsymbol{0}$, unless otherwise indicated explicitly. We note that $\boldsymbol{F}, \boldsymbol{F}'$ may be associated with bound states as well as with diffracted states, although energy cannot then be conserved in the bound states.

The final energy of an atom in a diffracted state, $\boldsymbol{F}$, is equal to its incident energy, E. The component of the final wave-vector of this atom parallel to the surface is $(\boldsymbol{K}+\boldsymbol{F})$, and it follows from (2.10) and (2.18) that k_{Fz} may be interpreted as the magnitude of the component normal to the surface.

Therefore, if, for a particular $\boldsymbol{G}$, we obtain $k_{Gz}^2 \geqslant 0$ from (2.10), this $\boldsymbol{G}$ is associated with a diffracted state and $\boldsymbol{F} \equiv \boldsymbol{G}$; if, on the other hand, $k_{Gz}^2 < 0$, this $\boldsymbol{G}$ is not associated with a diffracted state and there is no $\boldsymbol{F}$ equal to $\boldsymbol{G}$. Combining this result with (2.8) and (2.10), we obtain the condition for a diffracted state:

$$k_{Fz}^2 = k_z^2 - F^2 - 2\boldsymbol{K}\cdot\boldsymbol{F} \geqslant 0. \tag{2.19}$$

To simplify the notation slightly, we note that q in (2.16b) may stand for k_{Fz}, and that the following definitions may be made without ambiguity:

$$\phi_F \equiv \phi_q, \quad \xi_F \equiv \xi_q, \quad \text{etc.} \quad \text{if} \quad q = k_{Fz}. \tag{2.20}$$

For example, ξ_0 stands for ξ_q where $q = k_z = k_{0z}$.

3. Derivation of the scattering equations

3.1. General formalism

Ψ_G is expanded in terms of the ϕ_α as follows:

$$\Psi_G = \sum_\alpha c_{G\alpha}\, \phi_\alpha. \tag{3.1}$$

Substituting (3.1) into (2.11), we obtain

$$\sum_\alpha c_{G\alpha}(k_{Gz}^2 - \alpha^2)\, \phi_\alpha = (2M/\hbar^2) \sum_{G' \neq G} \sum_\alpha c_{G'\alpha}\, v_{G-G'}\, \phi_\alpha. \tag{3.2}$$

Multiplying both sides of (3.2) by $\phi_\beta^* (= \phi_\beta)$ and integrating over z in the usual manner, we obtain

$$c_{G\alpha}(k_{Gz}^2 - \alpha^2) = (2M/\hbar^2) \sum_{G' \neq G} \sum_\beta c_{G'\beta}(\beta|v_{G-G'}|\,\alpha), \tag{3.3}$$

where the matrix element is defined by

$$(\beta|v_G|\,\alpha) = \lim_{L\to\infty} \int_{-\frac{1}{2}L}^{+\frac{1}{2}L} \phi_\beta^*(z)\, v_G(z)\, \phi_\alpha(z)\, \mathrm{d}z. \tag{3.4}$$

Eq. (3.3) determines $c_{G\alpha}$ uniquely except where $\alpha = k_{Gz}$, when the ambiguity is resolved by demanding that $\Psi(\boldsymbol{r})$ describe an incoming plane wave of wave-vector $\boldsymbol{k}$ and outgoing scattered waves. We obtain

$$c_{G\alpha} \exp(-\mathrm{i}\xi_0) = \delta_{\alpha,0}\, \delta_{G,0} + (2M/\hbar^2)\,(k_{Gz}^2 - \alpha^2 + \mathrm{i}\varepsilon)^{-1}\,(\boldsymbol{G}\,\alpha|t|\,\boldsymbol{0}\,k_z), \tag{3.5}$$

where $\varepsilon > 0$ and we ultimately take the limit as $\varepsilon \to 0$, and where $(\boldsymbol{G}\,\alpha|t|\,\boldsymbol{0}\,k_z)$ is a t-matrix[13]), defined by

$$(\boldsymbol{G}\alpha|t|\,\boldsymbol{0}\,k_z)\exp(\mathrm{i}\xi_0) = \sum_{G' \neq G} \sum_\beta c_{G'\beta}(\alpha|v_{G-G'}|\,\beta). \tag{3.6}$$

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$\sum_{G\,\beta} c_{G'\beta} (\beta | v_{G-G'} | \alpha)$, (3.3)

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mit as $\varepsilon \to 0$, and where $(G\,\alpha|t|\,0\,k_z)$

$\sum_{G\,\beta} c_{G'\beta} (\alpha | v_{G-G'} | \beta)$. (3.6)

Substitution of (3.5) into (3.1) yields the following formula for the Ψ_G:

$$\Psi_G \exp(-i\xi_0) = \phi_0 \, \delta_{G,0} + \frac{2M}{\hbar^2} \sum_{\alpha} \frac{(G\,\alpha |t| \, 0 \, k_z) \, \phi_\alpha}{(k_{Gz}^2 - \alpha^2 + i\varepsilon)}, \tag{3.7}$$

where the equation for the t-matrix is obtained by substituting for $c_{G'\beta}$ in (3.6) from (3.5):

$$(G\,\alpha |t| \, 0 \, k_z) = (\alpha | v_G | \, k_z)(1 - \delta_{G,0}) + \frac{2M}{\hbar^2} \sum_{G' \neq G} \sum_{\beta} \frac{(\alpha | v_{G-G'} | \beta)(G' \, \beta |t| \, 0 \, k_z)}{(k_{G'z}^2 - \beta^2 + i\varepsilon)}. \tag{3.8}$$

Let us consider the summation over continuum states in (3.7):

$$S_1 \equiv \sum_{q} \frac{(G\,q |t| \, 0 \, k_z) \, \phi_q}{(k_{Gz}^2 - q^2 + i\varepsilon)}. \tag{3.9}$$

It is shown in Appendix A that the following results may be considered as exact:

$$k_{Gz}^2 < 0: \quad S_1(z \to \infty) = 0, \tag{3.10a}$$

$$k_{Gz}^2 > 0: \quad S_1(z \to \infty) = -(iL^{\frac{1}{2}}/2k_{Fz})(F\,k_{Fz} |t| \, 0 \, k_z) \exp[i(k_{Fz} z + \xi_F)], \tag{3.10b}$$

where F is used instead of G to emphasize that $k_{Gz}^2 > 0$ implies that $G = F$ is associated with a final diffracted state; see (2.19). It follows that $\Psi_F(z \to \infty)$, which is the asymptotic form as $z \to \infty$ of the diffracted beam F, is given essentially by the t-matrix, defined by (3.6) and (3.8).

3.2. Further development of notation

We now introduce dimensionless quantities, in terms of which our results may be conveniently expressed. These quantities are written in terms of two parameters, an inverse-length parameter, denoted by a, and an energy parameter, denoted by D. For example, these two parameters could be (and will be later) Morse interaction potential parameters[14]). Keeping, where convenient, to the notation of Lennard-Jones and his coworkers[12]), the following definitions are made:

$$\mu_G \equiv k_{Gz}/a, \quad \mu_0 \equiv k_z/a, \quad \text{etc.}, \tag{3.11}$$

$$d^2 \equiv 2MD/\hbar^2 a^2, \tag{3.12}$$

and

$$\lambda_m^G \equiv 2M(E - E_{mG})/\hbar^2 a^2. \tag{3.13}$$

Dimensionless matrix elements are defined as follows for $G \neq G'$:

$$A_{GG'}^{GG'} = A_{FF'}^{FF'} = \frac{aL}{4(\mu_F \mu_{F'})^{\frac{1}{2}}} \frac{d^2}{D} (k_{Fz} | v_{F-F'} | k_{F'z}), \tag{3.14}$$

$$A_{Gm}^{GG'} = A_{Fm}^{FG'} = \frac{(aL)^{\frac{1}{2}}}{2\mu_F^{\frac{1}{2}}} \frac{d^2}{D} (k_{Fz} | v_{F-G'} | m), \tag{3.15}$$

$$A_{mG'}^{GG'} = A_{mF}^{GF} = \frac{(aL)^{\frac{1}{2}}}{2\mu_F^{\frac{1}{2}}} \frac{d^2}{D} (m | v_{G-F} | k_{Fz}), \tag{3.16}$$

and

$$A_{mn}^{GG'} = \frac{d^2}{D} (m | v_{G-G'} | n), \tag{3.17}$$

where a G or F subscript on A stands for state k_{Gz} or k_{Fz}. Dimensionles[s] t-matrix elements are defined in a similar manner:

$$D_G^G = D_F^F = \frac{aL}{4(\mu_0 \mu_F)^{\frac{1}{2}}} \frac{d^2}{D} (F\, k_{Fz} | t | 0\, k_z) \tag{3.18}$$

and

$$D_G^m = \frac{\mathrm{i}(aL)^{\frac{1}{2}}}{2\lambda_m^G \mu_0^{\frac{1}{2}}} \frac{d^2}{D} (G\, m | t | 0\, k_z), \tag{3.19}$$

where a G or F superscript on D stands for state k_{Gz} or k_{Fz}. The asymptoti[c] form as $z \to \infty$ of the wave-function is now written explicitly in terms of th[e] dimensionless quantities D_G^z by use of (3.10):

$$L^{\frac{1}{2}} \Psi_0(z \to \infty) = \exp(-\mathrm{i}k_z z) + (1 - 2\mathrm{i}D_0^0) \exp[\mathrm{i}(k_z z + 2\xi_0)], \tag{3.20}$$

and

$$(L\mu_F/\mu_0)^{\frac{1}{2}} \Psi_F(z \to \infty) = -2\mathrm{i}\, D_F^F \exp[\mathrm{i}(k_{Fz} z + \xi_0 + \xi_F)]. \tag{3.21}$$

The part, $c_{Gm}\phi_m$, denoted here by Ψ_G^m, of Ψ_G associated with the bound stat[e] m may be written explicitly in terms of D_G^m:

$$(aL/\mu_0)^{\frac{1}{2}} \Psi_G^m(z) = -2\mathrm{i}\, D_G^m \phi_m(z) \exp(\mathrm{i}\xi_0). \tag{3.22}$$

3.3. Approximate scattering equations

In order to develop an approximate solution of the t-matrix eq. (3.8), w[e] consider the summation over continuum states therein:

$$S_2 \equiv \sum_q \frac{(\alpha | v_{G-G'} | q)(G'\, q | t | 0\, k_z)}{(k_{G'z}^2 - q^2 + \mathrm{i}\varepsilon)}. \tag{3.23}$$

The work so far has been *exact*; for example, Ψ_G is given exactly by (3.1[

If (3.3) is solved for $c_{G\alpha}$, and (3.8) is the exact t-matrix equation. However, unlike the summation S_1 in (3.9), the summation S_2 cannot be done exactly, and some approximation is necessary. The approximation used here is discussed in Appendix B, and amounts to calculating S_2 by keeping only the imaginary part of $(k_{G'z}^2 - q^2 + \mathrm{i}\varepsilon)^{-1}$, that is $-\mathrm{i}\pi\delta(k_{G'z}^2 - q^2)$. The result is

$$k_{G'z}^2 < 0: \quad S_2 \simeq 0, \tag{3.24a}$$

$$k_{G'z}^2 > 0: \quad S_2 \simeq -(\mathrm{i}L/4k_{Fz})(\alpha\,|v_{G-F}|\,k_{Fz})(F\,k_{Fz}\,|t|\,\mathbf{0}\,k_z), \tag{3.24b}$$

where F is used instead of G' for the reason stated just after (3.10b). Using this approximation in (3.8), we obtain the following approximate t-matrix equation, written in terms of the D_G^α defined by (3.18) and (3.19):

$$\mathrm{i}\,\lambda_\alpha^G\, D_G^\alpha = -A_{\alpha 0}^{G0}(1 - \delta_{G,0}) + \mathrm{i} \sum_{G' \neq G} \sum_{\beta} A_{\alpha\beta}^{GG'}\, D_{G'}^\beta, \tag{3.25}$$

where λ_G^G, as yet undefined, is defined for convenience by

$$\lambda_G^G = \mathrm{i}\,. \tag{3.26}$$

In practice, the calculation would be restricted to a consideration of, say, R non-zero reciprocal lattice vectors and B bound states, resulting in, say, the specular beam plus N other diffracted beams. [R is even because reciprocal lattice vectors must be chosen in pairs. If G is chosen, then in order that $v(r)$ be real it follows from (2.5) that $-G$ must be chosen also; the reality of $v(r)$ is then assured because it follows from (2.4) that $v_G = v_{-G}^*$.] To proceed, it is convenient to reduce the number of equations in (3.25) by eliminating D_0^α from the set; we have

$$\lambda_\alpha^0\, D_0^\alpha = \sum_{G' \neq 0} \sum_{\beta} A_{\alpha\beta}^{0G'}\, D_{G'}^\beta\,. \tag{3.27}$$

Substituting (3.27) into the right hand side of (3.25) for $G \neq 0$, we obtain the following $(N + BR)$ simultaneous equations for the remaining $D_G^\beta\,(G \neq 0)$:

$$\sum_{G' \neq 0} \sum_{\beta} X_{\alpha\beta}^{GG'}\, D_{G'}^\beta = A_{\alpha 0}^{G0} \begin{cases} G = F = 1, 2, \ldots, N;\ \beta = G = F, \\ G = 1, 2, \ldots, R;\ \beta = m = 1, 2, \ldots, B, \end{cases} \tag{3.28}$$

where

$$X_{\alpha\beta}^{GG'} \equiv A_{\alpha 0}^{G0}\, A_{0\beta}^{0G'} + \mathrm{i}\, A_{\alpha\beta}^{GG'} + \mathrm{i} \sum_m A_{\alpha m}^{G0}\, A_{m\beta}^{0G'} / \lambda_m^0, \tag{3.29}$$

where the $A_{\alpha\beta}^{GG}$, which are as yet undefined, are defined for convenience as follows:

$$A_{\alpha\alpha}^{GG} = -\lambda_\alpha^G, \tag{3.30a}$$

and

$$A_{\alpha\beta}^{GG} = 0 \quad \text{if} \quad \alpha \neq \beta\,. \tag{3.30b}$$

We may note that, with these definitions, our approximate t-matrix equation (3.25) may be written

$$\mathrm{i}\sum_{G'}\sum_{\beta} A_{\alpha\beta}^{GG'} D_{G'}^{\beta} = A_{\alpha 0}^{G0}(1-\delta_{G,0}). \tag{3.31}$$

The $X_{\beta\alpha}^{GG}$, for example, are given by

$$X_{FF}^{GG} = |A_{F0}^{G0}|^2 + 1 + \mathrm{i}\sum_m |A_{Fm}^{G0}|^2/\lambda_m^0, \tag{3.32a}$$

$$X_{mm}^{GG} = |A_{m0}^{G0}|^2 - \mathrm{i}\lambda_m^G + \mathrm{i}\sum_n |A_{mn}^{G0}|^2/\lambda_m^0, \tag{3.32b}$$

$$X_{\alpha\beta}^{GG} = A_{\alpha 0}^{G0} A_{0\beta}^{0G} + \mathrm{i}\sum_m A_{\alpha m}^{G0} A_{m\beta}^{0G}/\lambda_m^0 \quad \text{if} \quad \alpha \neq \beta. \tag{3.32c}$$

In fact, it is almost always a good approximation to set $\lambda_m^0 = \infty$, when the disappearance of the last terms of X in (3.29) and (3.32) causes considerable simplification. Reasons for this are discussed further in section 4.3.

We may emphasize that D_0^0 and D_0^m, which appear, respectively, in the expression (3.20) for $\Psi_0(z\to\infty)$ and in (3.22) for $\Psi_0^m(z)$, are obtained in terms of the $D_G^{\alpha}(G\neq 0)$ in (3.28) from (3.27); that is,

$$D_0^0 = -\mathrm{i}\sum_{G\neq 0}\sum_{\alpha} A_{0\alpha}^{0G} D_G^{\alpha}, \tag{3.33}$$

and

$$D_0^m = \sum_{G\neq 0}\sum_{\alpha} A_{m\alpha}^{0G} D_G^{\alpha}/\lambda_m^0. \tag{3.34}$$

We note that D_0^m vanishes if $\lambda_m^0 = \infty$.

3.4. Intensities and Unitarity

An "intensity", R_F, is defined for each of the outgoing (specular and diffracted) beams:

$$R_F \equiv (L\mu_F/\mu_0)\,|\Psi_F^+(z\to\infty)|^2, \tag{3.35}$$

where Ψ_F^+ denotes the outgoing part of Ψ_F; it follows from (3.20) and (3.21) that

$$R_F = |\delta_{F,0} - 2\mathrm{i}D_F^F|^2. \tag{3.36}$$

The intensities are defined so that

$$R_F = \frac{\text{flux of atoms in the diffracted beam } F}{\text{incident flux of atoms}}, \tag{3.37}$$

and it follows that the R_F must satisfy the relation

$$\sum_F R_F = 1. \tag{3.38}$$

. our approximate t-matrix equation

$$^{G0}_{\alpha 0}(1-\delta_{G,0})\,. \qquad (3.31)$$

$$^{G0}_{Fm}|^2/\lambda^0_m\,, \qquad (3.32a)$$

$$|A^{G0}_{mn}|^2/\lambda^0_m\,, \qquad (3.32b)$$

$$A^{0G}_{m\beta}/\lambda^0_m \quad \text{if} \quad \alpha \neq \beta\,. \qquad (3.32c)$$

oximation to set $\lambda^0_m = \infty$, when the 3.29) and (3.32) causes considerable ssed further in section 4.3. hich appear, respectively, in the ex- 2) for $\Psi^m_0(z)$, are obtained in terms hat is,

$$A^{0G}_{0\alpha}\, D^\alpha_G\,, \qquad (3.33)$$

$$^{G}_{\alpha}\, D^\alpha_G/\lambda^0_m\,. \qquad (3.34)$$

n of the outgoing (specular and dif-

$$_F^+(z\to\infty)|^2\,, \qquad (3.35)$$

μ_F; it follows from (3.20) and (3.21)

$$- 2iD^F_F|^2\,. \qquad (3.36)$$

e diffracted beam F

ux of atoms , (3.37)

he relation

$$1\,. \qquad (3.38)$$

The relation (3.38) corresponds to the unitarity condition of the t-matrix theory[13]; it is proved from the above work in Appendix C.

4. Application to some special cases

It is instructive and interesting to illustrate the results of section 3 by specializing them to cases in which only a small number, R, of non-zero reciprocal lattice vectors and a small number, B, of bound states are considered. This specialization implies also a small number, $N+1$, of outgoing beams, because $N \leqslant R$.

4.1. $R=0$, $B=0$, $N=0$

This is the simplest possible case, that of complete specular reflection; we obtain

$$L^{\frac{1}{2}}\,\Psi_0(z\to\infty) = \exp(-\,\mathrm{i}k_z z) + \exp[\mathrm{i}(k_z z + 2\xi_0)]\,, \qquad (4.1)$$

and

$$R_0 = 1\,. \qquad (4.2)$$

4.2. $R=2$, $B=0$, $N=1$

Here we have just two reciprocal lattice vectors, one of which is linked to a diffracted beam, with no bound states

$$L^{\frac{1}{2}}\,\Psi_0(z\to\infty) = \exp(-\,\mathrm{i}k_z z) + \exp(\mathrm{i}k_z z)\left[\frac{1-|A^{F0}_{F0}|^2}{1+|A^{F0}_{F0}|^2}\right], \qquad (4.3)$$

$$(L\mu_F/\mu_0)^{\frac{1}{2}}\,\Psi_F(z\to\infty) = -\,\mathrm{i}\exp[\mathrm{i}(k_{Fz}z + \xi_0 + \xi_F)]\left[\frac{2A^{F0}_{F0}}{1+|A^{F0}_{F0}|^2}\right], \qquad (4.4)$$

$$R_F = 1 - R_0 = \left[\frac{2|A^{F0}_{F0}|}{1+|A^{F0}_{F0}|^2}\right]^2. \qquad (4.5)$$

4.3. $R=2$, $B=1$, $N=0$, $\lambda^0_m = \infty$

The only outgoing beam is the specular beam, but passages through a single bound state are allowed by two reciprocal lattice vectors. The assumption that λ^0_m is large results in considerable simplification, and is generally valid because it follows from (2.8), (2.17), (2.18) and (3.13) that

$$a^2\lambda^0_m = k_z^2 - 2ME_m/\hbar^2\,. \qquad (4.6)$$

Now $k_z^2 \geqslant 0$ and $E_m \leqslant 0$, and the only conditions under which λ^0_m could be small are either very low incident energy or very glancing incidence (k_z^2 small) coupled with the existence of a bound state very near the top of the potential well ($-E_m$ small).

$$L^{\frac{1}{2}}\,\Psi_0(z\to\infty) = \exp(-\mathrm{i}k_z z) + \exp[\mathrm{i}(k_z z + 2\xi_0)] \times \\ \times \left[\frac{1 - \mathrm{i}\,|A^{G0}_{m0}|^2\,(1/\lambda^G_m + 1/\lambda^{-G}_m)}{1 + \mathrm{i}\,|A^{G0}_{m0}|^2\,(1/\lambda^G_m + 1/\lambda^{-G}_m)}\right], \tag{4.7}$$

$$(aL/\mu_0)^{\frac{1}{2}}\,\Psi^m_G(z) = \exp(\mathrm{i}\xi_0)\,\phi_m(z)\left[\frac{2A^{G0}_{m0}/\lambda^G_m}{1 + \mathrm{i}\,|A^{G0}_{m0}|^2\,(1/\lambda^G_m + 1/\lambda^{-G}_m)}\right], \tag{4.8}$$

$$R_0 = 1\,. \tag{4.9}$$

We note that we cannot in general assume that λ^G_m or λ^{-G}_m is large as we did in (4.6) for λ^0_m. In fact, it follows from (3.13) that λ^G_m is a measure of how far the incident state is from resonance with a bound state m through the reciprocal lattice vector G; for example, $\lambda^G_m = 0$ at *exact* resonance. The result that λ^0_m can never vanish follows from the fact that the incident state cannot resonate exactly with a bound state without participation of a non-zero reciprocal lattice vector.

4.4. $R = R'$, $\lambda^0_m = \infty$

A general result for B bound states and $N(\leqslant R')$ diffracted beams can be written in simple form with the (severe) restriction that the R' non-zero reciprocal lattice vectors are chosen so that none can be written as a difference of two others. With this restriction, the second term of X in (3.29) is zero (there is no reciprocal lattice vector $G - G'$). As in the previous section, we set $\lambda^0_m = \infty$ for simplicity, when only the first term of X in (3.29) remains

$$L^{\frac{1}{2}}\,\Psi_0(z\to\infty) = \exp(-\mathrm{i}k_z z) + \exp[\mathrm{i}(k_z z + 2\xi_0)]\,(2 - \Delta)/\Delta\,, \tag{4.10}$$

$$(L\mu_F/\mu_0)^{\frac{1}{2}}\,\Psi_F(z\to\infty) = -\,\mathrm{i}\exp[\mathrm{i}(k_{Fz}z + \xi_0 + \xi_F)]\,2A^{F0}_{F0}/\Delta\,, \tag{4.11}$$

and

$$(aL/\mu_0)^{\frac{1}{2}}\,\Psi^m_G(z) = \exp(\mathrm{i}\xi_0)\,\phi_m(z)\,2A^{G0}_{m0}/\lambda^G_m\Delta\,, \tag{4.12}$$

where

$$\Delta \equiv 1 + \sum_{F\neq 0} |A^{F0}_{F0}|^2 + \mathrm{i}\sum_{G\neq 0}\sum_m |A^{G0}_{m0}|^2/\lambda^G_m\,. \tag{4.13}$$

$$R_F = 4\,|A^{F0}_{F0}/\Delta|^2\,, \tag{4.14a}$$

$$R_0 = 1 - \sum_{F\neq 0} R_F\,. \tag{4.14b}$$

5. The thermally-averaged potential energy function

5.1. General considerations

Let us consider the details of the calculation of the thermally-averaged potential energy function, $v(\boldsymbol{r})$, from the instantaneous potential function

$$\text{xp}\left[\mathrm{i}(k_z z + 2\xi_0)\right] \times$$

$$\frac{1/\lambda_m^G + 1/\lambda_m^{-G})}{1/\lambda_m^G + 1/\lambda_m^{-G})}\Bigg], \qquad (4.7)$$

$$- \frac{2A_{m0}^{G0}/\lambda_m^G}{1 + \mathrm{i}\,|A_{m0}^{G0}|^2\,(1/\lambda_m^G + 1/\lambda_m^{-G})}\Bigg], \qquad (4.8)$$

(4.9)

me that λ_m^G or λ_m^{-G} is large as we did
3.13) that λ_m^G is a measure of how far
h a bound state m through the reci-
${}_m^G=0$ at *exact* resonance. The result
he fact that the incident state cannot
ithout participation of a non-zero

nd $N(\leqslant R')$ diffracted beams can be
e) restriction that the R' non-zero
hat none can be written as a differ-
n. the second term of X in (3.29) is
$G-G'$). As in the previous section,
the first term of X in (3.29) remains

$$\text{xp}\left[\mathrm{i}(k_z z + 2\xi_0)\right](2-\Delta)/\Delta\,, \qquad (4.10)$$

$$+ \xi_0 + \xi_F)\right] 2A_{F0}^{F0}/\Delta\,, \qquad (4.11)$$

$$\xi_0)\,\phi_m(z)\,2A_{m0}^{G0}/\lambda_m^G\Delta\,, \qquad (4.12)$$

$$\mathrm{i} \sum_{G\neq 0} \sum_m |A_{m0}^{G0}|^2/\lambda_m^G\,. \qquad (4.13)$$

(4.14a)

(4.14b)

potential energy function

lculation of the thermally-averaged
he instantaneous potential function,

$V(r, u)$, via (2.1). The function $V(r, u)$ is itself assumed to be obtained by a summation, over all atoms of the solid, of a pairwise potential energy function, denoted by $U(r-r_n-u_n)$, where r is the gas atom position, r_n is the equilibrium position of the solid atom n and u_n its displacement from equilibrium. Hence,

$$V(r, u) = \sum_n U(r - r_n - u_n)\,. \qquad (5.1)$$

We recall the notation (2.3) and similarly define

$$r_n = (R_n, z_n) \qquad (5.2)$$

for the equilibrium positions and

$$p = (P, p_z) \qquad (5.3)$$

for wave-vectors. We write

$$V(r, u) = (L/2\pi)^3 \sum_n \int U_p \exp\left[\mathrm{i}p\cdot(r - r_n - u_n)\right] \mathrm{d}^3 p\,, \qquad (5.4)$$

where

$$U_p \equiv L^{-3} \int U(r) \exp(-\,\mathrm{i}p\cdot r)\, \mathrm{d}^3 r\,, \qquad (5.5)$$

and integrals are understood to be between the limits $\pm\infty$ unless otherwise indicated. Therefore, the thermally-averaged value, $v(r)$, of $V(r, u)$ is given by

$$v(r) = (L/2\pi)^3 \sum_n \int U_p \exp\left[\mathrm{i}p\cdot(r - r_n)\right] \langle \exp(-\,\mathrm{i}p\cdot u_n)\rangle\, \mathrm{d}^3 p\,. \qquad (5.6)$$

It is a well-known result that[15])

$$\langle \exp(\mathrm{i}p\cdot u_n)\rangle = \exp\langle -\tfrac{1}{2}(p\cdot u_n)^2\rangle \equiv \exp\left[-\,W(n, p)\right], \qquad (5.7)$$

where W is a Debye–Waller exponent:

$$W(n, P, p_z) \equiv \langle \tfrac{1}{2}(p\cdot u_n)^2\rangle \qquad (5.8)$$

$$= \tfrac{1}{2}(p_x^2\langle u_{xn}^2\rangle + p_y^2\langle u_{yn}^2\rangle + p_z^2\langle u_{zn}^2\rangle)\,. \qquad (5.9)$$

From (2.3), (5.3), (5.6) and (5.7), we have

$$v(r) = (L/2\pi)^3 \sum_n \int \mathrm{d}^2 P\, \mathrm{d}q\, \times$$

$$\times\, U_{P,q} \exp\left[\mathrm{i}P\cdot(R - R_n)\right] \exp\left[\mathrm{i}q(z - z_n)\right] \exp\left[-\,W(n, P, q)\right], \qquad (5.10)$$

where q stands for the dummy variable p_z, and where both z_n and $W(n, p, q)$ are understood to be independent of n_x and n_y.

Using the result that

$$\sum_{n_x}\sum_{n_y} \exp(\mathrm{i}\boldsymbol{P}\cdot\boldsymbol{R}_n) = N_s(2\pi/L)^2 \sum_{\boldsymbol{G}} \delta(\boldsymbol{P}-\boldsymbol{G}), \tag{5.11}$$

where N_s is the number of surface atoms, we obtain

$$v(\boldsymbol{r}) = N_s(L/2\pi)\sum_{\boldsymbol{G}} \exp(\mathrm{i}\boldsymbol{G}\cdot\boldsymbol{R}) \times \sum_{n_z}\int \mathrm{d}q\, U_{\boldsymbol{G},q} \exp(\mathrm{i}qz)\exp(-\mathrm{i}qz_n)\exp[-W(\boldsymbol{n},\boldsymbol{G},q)]. \tag{5.12}$$

From (2.5 and (5.12), we obtain

$$v_{\boldsymbol{G}}(z) = (N_s L/2\pi)\int \exp(\mathrm{i}qz)\, U_{\boldsymbol{G},q}\sum_{n_z}\exp[-W(\boldsymbol{n},\boldsymbol{G},q)]\exp(-\mathrm{i}qz_n)\,\mathrm{d}q. \tag{5.13}$$

When $W=0$, v is to be interpreted as V:

$$V_{\boldsymbol{G}}(z) = N_s(L/2\pi)\int \exp(\mathrm{i}qz)\, U_{\boldsymbol{G},q}\sum_{n_z}\exp(-\mathrm{i}qz_n)\,\mathrm{d}q. \tag{5.14}$$

If we define

$$V_{\boldsymbol{G},q} = L^{-1}\int V_{\boldsymbol{G}}(z)\exp(-\mathrm{i}qz)\,\mathrm{d}z, \tag{5.15}$$

it follows from (5.14) that

$$V_{\boldsymbol{G},q} = N_s U_{\boldsymbol{G},q}\sum_{n_z}\exp(-\mathrm{i}qz_n). \tag{5.16}$$

For simplicity, we make the approximation that W is independent of n_z, replacing $W(\boldsymbol{n},\boldsymbol{G},q)$ by $W(\boldsymbol{G},q)$:

$$W(\boldsymbol{G},q) \equiv \tfrac{1}{2}(G^2\langle u_x^2\rangle + q^2\langle u_z^2\rangle), \tag{5.17}$$

where we have set

$$\langle u_{xn}^2\rangle = \langle u_{yn}^2\rangle = \langle u_x^2\rangle \quad \text{for all } \boldsymbol{n}, \tag{5.18a}$$

and

$$\langle u_{zn}^2\rangle = \langle u_z^2\rangle \quad \text{for all } \boldsymbol{n}. \tag{5.18b}$$

With the approximations (5.17) and (5.18), it follows from (5.13) and (5.16) that

$$v_{\boldsymbol{G}}(z) = \exp(-\tfrac{1}{2}G^2\langle u_x^2\rangle)(L/2\pi)\int \exp(\mathrm{i}qz)\, V_{\boldsymbol{G},q}\exp(-\tfrac{1}{2}q^2\langle u_z^2\rangle)\,\mathrm{d}q. \tag{5.19}$$

Substituting for $V_{\boldsymbol{G},q}$ in (5.19) from (5.15) and carrying out the q-integration, we obtain

$$v_G(z) = \frac{\exp(-\frac{1}{2}G^2\langle u_x^2\rangle)}{(2\pi\langle u_z^2\rangle)^{\frac{1}{2}}} \int V_G(z')\exp\left(-\frac{(z'-z)}{2\langle u_z^2\rangle}\right)\mathrm{d}z' . \qquad (5.20)$$

5.2. The Morse potential representation

We represent $V_0(z)$ by a Morse potential[14]), and $V_G(z)$ by the corresponding exponential repulsion if $G\neq 0$:

$$V_0(z) = D'\{\exp[2a(z'_m - z)] - 2\exp[a(z'_m - z)]\}, \qquad (5.21)$$

$$V_G(z) = \kappa'_G D' \exp[2a(z'_m - z)] \quad \text{if } \boldsymbol{G} \neq \boldsymbol{0}. \qquad (5.22)$$

Let us consider the general term

$$V_G(z) = A\exp(-bz). \qquad (5.23)$$

Inserting (5.23) into (5.20), we obtain

$$v_G(z) = \exp(-\tfrac{1}{2}G^2\langle u_x^2\rangle)\exp(\tfrac{1}{2}b^2\langle u_z^2\rangle)\,V_G(z). \qquad (5.24)$$

Therefore, with the expressions (5.21) and (5.22), our thermally-averaged $v_0(z)$ remains a Morse potential, with the same a but with modified D and z_m; our thermally-averaged $v_G(z)$, for $\boldsymbol{G}\neq\boldsymbol{0}$, remains an exponential repulsion, with modified κ_G, D and z_m:

$$v_0(z) = D\{\exp[2a(z_m - z)] - 2\exp[a(z_m - z)]\}. \qquad (5.25)$$

and

$$v_G(z) = \kappa_G D\exp[2a(z_m - z)] \quad \text{for } \boldsymbol{G}\neq\boldsymbol{0}, \qquad (5.26)$$

where

$$\kappa_G \equiv \kappa'_G \exp(-\tfrac{1}{2}G^2\langle u_x^2\rangle), \qquad (5.27)$$

$$D \equiv D'\exp(-a^2\langle u_z^2\rangle), \qquad (5.28)$$

and

$$z_m \equiv z'_m + \tfrac{3}{2}a\langle u_z^2\rangle. \qquad (5.29)$$

5.3. Eigenstates and matrix elements

With $v_0(z)$ given by the Morse potential (5.25), the eigenstates ϕ_α, defined by (2.12)–(2.16), are[16,17])

$$L^{\frac{1}{2}}\phi_q(z) = \left|\frac{\Gamma(\frac{1}{2} - d + \mathrm{i}\mu)}{\Gamma(2\mathrm{i}\mu)}\right| \zeta^{-\frac{1}{2}} W_{d,\mathrm{i}\mu}(\zeta), \qquad (5.30)$$

and

$$a^{-\frac{1}{2}}\phi_n(z) = \left[\frac{(2d-1-2n)\,n!}{(2d-1-n)\,!^3}\right]^{\frac{1}{2}} \mathrm{e}^{-\frac{1}{2}\zeta}\zeta^{d-\frac{1}{2}-n} L^{2d-1-2n}_{2d-1-n}(\zeta), \qquad (5.31)$$

where μ is defined to conform to the notation (3.11),

$$\mu = q/a\,, \tag{5.32}$$

ζ is defined by

$$\zeta = 2d \exp[a(z_m - z)]\,, \tag{5.33}$$

and where $W_{a,b}(\zeta)$ and $L_b^a(\zeta)$ are, respectively, the confluent hypergeometric function[16]) of ξ and the generalized Laguerre polynomial function[17]) of ζ. The eigenvalues, E_α, are given by (2.13) and (2.14) where k_n for a bound state is given by

$$k_n = a(d - \tfrac{1}{2} - n), \quad n = 0, 1, 2, \ldots \quad (n \leqslant d - \tfrac{1}{2}). \tag{5.34}$$

With the above representation of the potentials $v_G(z)$, the matrix elements (3.14)–(3.17) may be expressed as follows

$$\begin{aligned}\frac{A_{FF'}^{FF'}}{\kappa_{F-F'}} &= \frac{\pi}{4}\frac{[\sinh(2\pi\mu_F)\sinh(2\pi\mu_{F'})]^{\frac{1}{2}}}{[\cosh(2\pi\mu_F) - \cosh(2\pi\mu_{F'})]} \times \\ &\times \left[(\mu_F^2 - \mu_{F'}^2 + 2d)\left|\frac{\Gamma(\frac{1}{2} - d + \mathrm{i}\mu_{F'})}{\Gamma(\frac{1}{2} - d + \mathrm{i}\mu_F)}\right| + \right. \\ &\left. + (\mu_F^2 - \mu_{F'}^2 - 2d)\left|\frac{\Gamma(\frac{1}{2} - d + \mathrm{i}\mu_F)}{\Gamma(\frac{1}{2} - d + \mathrm{i}\mu_{F'})}\right|\right],\end{aligned} \tag{5.35}$$

$$\begin{aligned}\frac{A_{Fm}^{FG}}{\kappa_{F-G}} = \frac{A_{mF}^{GF}}{\kappa_{G-F}} &= \frac{\pi^{\frac{1}{2}}}{4}\left[\frac{(2d - 2m - 1)}{m!\,(2d - m - 1)\,!}\right]^{\frac{1}{2}} \times \\ &\times \left[\frac{\sinh(2\pi\mu_F)}{\cosh(2\pi\mu_F) + \cos(2\pi d)}\right]^{\frac{1}{2}} \times \\ &\times (\mu_F^2 + (d - \tfrac{1}{2} - m)^2 + 2d)\,|\Gamma(\tfrac{1}{2} + d + \mathrm{i}\mu_F)|\,,\end{aligned} \tag{5.36}$$

$$\begin{aligned}\frac{A_{mn}^{GG'}}{\kappa_{G-G'}} &= \frac{(-)^{m-n}}{4}\left[\frac{(2d - m - 1)\,!\,m!}{(2d - n - 1)\,!\,n!}(2d - 2m - 1)(2d - 2n - 1)\right]^{\frac{1}{2}} \times \\ &\times [(m - n)(2d - m - n - 1) + 2d] \qquad \text{if } m \geqslant n\,.\end{aligned} \tag{5.37}$$

If $A_{mn}^{GG'}$ for $n > m$ is required, then m and n are interchanged in (5.37).

6. Discussion of the elastic scattering theory

6.1. Relationship to the distorted wave Born approximation

If the results of sections 3 and 4 are expanded to lowest order in the matrix elements, the first order (distorted wave Born approximation) results are otation (3.11),

$$a\,, \tag{5.32}$$

$$(z_m - z)]\,, \tag{5.33}$$

ctively, the confluent hypergeometric guerre polynomial function[17]) of ζ 3) and (2.14) where k_n for a bound

$$. \; 1, 2, \ldots \quad (n \leqslant d - \tfrac{1}{2})\,. \tag{5.34}$$

otentials $v_G(z)$, the matrix elements vs

$$\pi\mu_{F'})]^{\frac{1}{2}} \over (2\pi\mu_{F'})] \times$$

$$\frac{\tfrac{1}{2} - d + \mathrm{i}\mu_{F'})}{\tfrac{1}{2} - d + \mathrm{i}\mu_{F})} + \frac{- d + \mathrm{i}\mu_{F})}{- d + \mathrm{i}\mu_{F'})}\Bigg]\,, \tag{5.35}$$

$$\left[\frac{n-1)}{m-1)\,!}\right]^{\frac{1}{2}} \times \left[\frac{}{2\pi d)}\right]^{\frac{1}{2}} \times + 2d)\,|\Gamma(\tfrac{1}{2} + d + \mathrm{i}\mu_F)|\,, \tag{5.36}$$

$$2d - 2m - 1)(2d - 2n - 1)\Big]^{-\frac{1}{2}} \times \quad) + 2d] \qquad \text{if } m \geqslant n\,. \tag{5.37}$$

d n are interchanged in (5.37).

stic scattering theory

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panded to lowest order in the matrix ve Born approximation) results are

recovered. For example, from section 4.2 we obtain

$$R_0 \simeq 1 - 4X\,, \tag{6.1a}$$

and

$$R_F \simeq 4X\,, \tag{6.1b}$$

where

$$X \equiv |A_{F0}^{F0}|^2\,, \tag{6.2}$$

provided that $X \ll 1$. There is little difference between the first-order results (6.1) and our results (4.5) if $X \ll 1$, that is, if the matrix element modulus is "small"; of course, this is the motivation behind first order theory. The point here is that the present theory leads to sensible results no matter how large are the matrix element moduli.

For example, two particularly interesting results follow from (4.5): (i) for certain values of the matrix element A_{F0}^{F0}, the intensity of the specular beam is considerably less than that of the diffracted beam; indeed, if $|A_{F0}^{F0}| = 1$, the specular beam vanishes and all outgoing atoms pass into the diffracted beam: (ii) for *both* very small *and* very large values of $|A_{F0}^{F0}|$, the specular intensity approaches unity and, of course, has a minimum for intermediate $|A_{F0}^{F0}|$; for the special case (4.5), this minimum is zero, as observed in (i).

6.2. Resonances with bound states

A result of considerable importance concerns the case of "resonance" of the incident beam with a bound state; for $E = E_{mG}$ we obtain exact resonance, with $\lambda_m^G = 0$ from (3.13). It follows from the above results [for example, (4.13) and (4.14) and their generalizations] that, when exact resonance occurs, the intensity of the specular beam rises sharply, and that of each of the other beams falls. On the other hand, it has been known for some time that, experimentally, the intensity of the specular beam generally *falls* as resonance is approached[18,19]). This fall in the specular intensity is undoubtedly due to inelastic scattering of the gas beam, the probability of which is greatly increased if the gas atoms resonate into a bound state, because of the extra time they stay (while travelling over the surface in the bound state) in close proximity to the surface. The theory developed so far considers only elastic scattering, and all gas atoms are either specularly scattered or diffracted, independently of the time they spend in intermediate bound states. The above points regarding the effects of inelastic scattering are considered further in section 7.

6.3. Surface resonances

The phenomena which we call "surface resonances" are most easily discussed with reference to the actual forms, (5.35) and (5.36), of the matrix elements. These resonances refer to the behavior of the diffraction as a diffracted beam just appears above, or just disappears below, the surface. (We note from (2.19) and (3.11) that a diffracted beam is allowed if $\mu_G^2 > 0$, and is not allowed if $\mu_G^2 < 0$.) This behavior depends critically on d, the parameter defined by (3.12) where, of course, a and D are now the Morse potential parameters; two extreme types of behavior are possible, with a gradually-varying spectrum in between. We restrict attention for the moment to the example in section 4.4.

The first, and simpler, extreme type of behavior occurs in general when d is not nearly half an odd integer, say when $d \simeq$ integer. Then, $|A_{m0}^{G0}|^2/\lambda_m^G$ varies smoothly in general as μ_G^2 passes through zero, and $|A_{F0}^{F0}|^2 \to$ constant $\times\, \mu_F$ as $\mu_F^2 \to 0+$. It follows from (4.13) and (4.14) that, as a diffracted beam, say F', disappears, the intensity $R_{F'}$ falls rapidly, but smoothly, to zero, all the other intensities $R_F\,(F \neq F')$ increasing rapidly, but smoothly, to pick up on new curves.

As d becomes closer to half an odd integer, the behaviors of the R_F become more complicated. If

$$d = n + \tfrac{1}{2} + \delta_n\,, \tag{6.3}$$

where $|\delta_n|$ is small, the relevant matrix elements have the following forms for small $|\mu_G^2|$ or μ_F^2:

$$\frac{|A_{F0}^{F0}|^2}{\kappa_F^2} = \frac{\mu_F}{(\delta_n^2 + \mu_F^2)}\, X\,, \tag{6.4a}$$

and

$$\frac{|A_{n0}^{G0}|^2}{\kappa_G^2 \lambda_n^G} = \frac{2\delta_n}{(\delta_n^2 + \mu_G^2)}\, X\,, \tag{6.4b}$$

where

$$X \equiv \frac{\pi}{16} \coth(\pi\mu_0)\, \frac{(\mu_0^2 + 1 + 2n)^2}{n!^2}\, |\Gamma(n + 1 + \mathrm{i}\mu_0)|^2\,, \tag{6.4c}$$

and where we note that the bound state n does not exist unless $\delta_n \geqslant 0$. At $\delta_n = 0$ exactly, we obtain, again for small $|\mu_G^2|$ or μ_F^2:

$$|A_{F0}^{F0}|^2 \to \kappa_F^2 X/\mu_F \tag{6.5a}$$

and

$$|A_{n0}^{G0}|^2/\lambda_n^G \to 0\,. \tag{6.5b}$$

For this special extreme case (d = half an odd integer), nothing spectacular happens as one of the μ_G^2, say $\mu_{G'}^2$, increases through negative values to zero, but, for $\mu_{G'}^2 = \mu_{F'}^2 = 0$, $|A_{F'0}^{F'0}|^2$ tends to infinity and R_0 jumps discontinuously to unity, all the $R_F(F \neq 0)$ dropping to zero. R_0 falls and $R_F(F \neq 0)$ rises as $|A_{F'0}^{F'0}|^2$ decreases through moderate values, and in fact R_0 then displays a

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$$+ \delta_n , \quad (6.3)$$

ements have the following forms for

$$\frac{{}_F}{-\mu_F^2)} X , \quad (6.4a)$$

$$\frac{2\delta_n}{+\mu_G^2)} X , \quad (6.4b)$$

$$\frac{-2n)^2}{} |\Gamma(n+1+i\mu_0)|^2 , \quad (6.4c)$$

te n does not exist unless $\delta_n \geqslant 0$. At
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$$\kappa_F^2 X/\mu_F \quad (6.5a)$$

$$\to 0 . \quad (6.5b)$$

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minimum, $R_{F'}$ displaying a corresponding maximum; for smaller values of $|A^{F0}_{F'0}|^2$, R_0 increases rapidly to later pick up on a smooth curve, this increase being accompanied by a corresponding decrease of $R_{F'}$. If δ_n is not exactly zero, these results are somewhat modified, although the resonance phenomena persist provided that $|\delta_n|$ is not too large. Similar resonances as $\mu_G^2\to 0$ have been discussed by McRae[10]) for the case of low energy electron diffraction.

Fig. 1 illustrates the behavior of the intensities as functions of $\mu_{G'}^2$ where

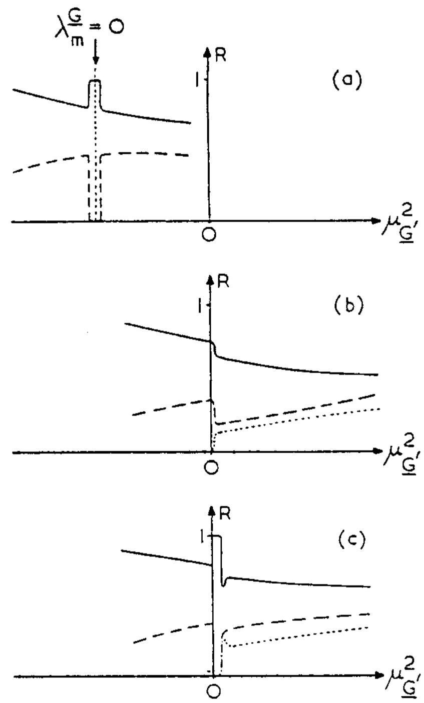

Fig. 1. The behavior of the intensities R_0(——), R_F(------) and $R_{F'}$(·····) as functions of $\mu^2{}_{G'}$ where some of the resonance phenomena, discussed in section 6, occur. (a) R_0 and R_F when a resonance with the bound state m occurs via the reciprocal lattice vector G for a special case of the type discussed in section 4.4. (b) R_0, $R_{F'}(F'=G')$ and $R_F(F\neq G')$ as the diffracted beam F' appears above the surface (at $\mu^2{}_{G'}=\mu^2{}_{F'}=0$) when $d\simeq$ integer. (c) The same as (b) when $d=$ half an odd integer.

some of these resonance phenomena occur. Fig. 1a shows R_0 and R_F when a resonance with the bound state m occurs via the reciprocal lattice vector G for a special case of the type discussed in section 4.4. Fig. 1b describes R_0, R_F $(F'=G')$ and $R_F(F\neq G')$ as the diffracted beam F' appears above the surface (at $\mu^2_{G'}=\mu^2_{F'}=0$) for a case in which the "surface resonance" described above does not occur (that is, $d \simeq$ integer, say). Fig. 1c illustrates the same case as does fig. 1b, except that now $d =$ half and odd integer exactly.

We note that these surface resonances, discussed here for $\mu_G^2 \to 0$, occur also when $\mu_0^2 \to 0$ that is, they occur as tangential incidence is approached. However, resonances of this type are not as important because the incidence must be too close to tangential to be feasible experimentally.

7. Extension to inelastic scattering

We consider in this section the effects of excitation and de-excitation of thermal vibrations in the solid by an impinging gas atom; the need to consider the thermal vibrations is already foreshadowed by our use of the thermally-averaged potential, v, in section 2. The formal theory is a direct generalization of that developed in sections 2 and 3, and many intermediate steps are omitted.

The wave-function, $\Psi(\boldsymbol{r}, \boldsymbol{u})$ may be expanded as follows:

$$\Psi(\boldsymbol{r}, \boldsymbol{u}) = \sum_{\boldsymbol{K}', \alpha, \nu} c_{\boldsymbol{K}', \alpha, \nu}\, \phi_\alpha(z)\, \mathrm{e}^{\mathrm{i}\boldsymbol{K}' \cdot \boldsymbol{R}}\, \Phi_\nu(\boldsymbol{u}). \tag{7.1}$$

where $\Phi_\nu(\boldsymbol{u})$ is a vibrational wave-function of the solid, ν runs over vibrational quantum numbers, and the sum over $\boldsymbol{K}'$ replaces that over $\boldsymbol{G}$ in (2.6). Of course, $\boldsymbol{K}'$ assumes all values and not just those $\boldsymbol{K} + \boldsymbol{G}$. We introduce a shorthand index, f or g, for all the quantum numbers $\boldsymbol{K}', \alpha, \nu$; we use g in general, and f when we wish to stress that we are dealing with a final outgoing state (this notation parallels the $\boldsymbol{F}, \boldsymbol{G}$ notation of section 3). The label 0 is reserved for the quantum numbers of the initial (or specular) state.

The analogue of (3.5) is

$$c_g\, \mathrm{e}^{-\mathrm{i}\xi_0} = \delta_{g,0} + (E_0 - E_g + \mathrm{i}\varepsilon)^{-1}\, t_{g0}, \tag{7.2}$$

where E_0 and E_g include the vibrational energies; the analogue of (3.6) is

$$t_{g0}\, \mathrm{e}^{\mathrm{i}\xi_0} = \sum_{g' \neq g} c_{g'} V_{gg'}. \tag{7.3}$$

Our t-matrix equation, the analogue of (3.8), is obtained by substituting for $c_{g'}$ in (7.3) from (7.2):

$$t_{g0} = V_{g0}(1 - \delta_{g,0}) + \sum_{g' \neq g} \frac{V_{gg'} t_{g'0}}{(E_0 - E_{g'} + \mathrm{i}\varepsilon)}. \tag{7.4}$$

The notation is further refined so that $g = b$ stands for a quantum number set associated with a bound state and $g = c$ with a continuum state; we note that f is always associated with a continuum state. Then, dimensionless quantities may be defined by direct analogy with (3.11)–(3.19) and (3.26).

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anded as follows:

$$z) \, e^{iK' \cdot R} \, \Phi_v(u) , \qquad (7.1)$$

n of the solid, v runs over vibra-
K' replaces that over G in (2.6).
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$$E_g + i\varepsilon)^{-1} \, t_{g0} , \qquad (7.2)$$

energies; the analogue of (3.6) is

$$V_{gg'} . \qquad (7.3)$$

.8), is obtained by substituting for

$$\frac{V_{gg'} t_{g'0}}{(E_0 - E_{g'} + i\varepsilon)} . \qquad (7.4)$$

$=b$ stands for a quantum number
with a continuum state; we note
uum state. Then, dimensionless
gy with (3.11)-(3.19) and (3.26).

Care must be taken over interpreting the definitions, some of which are presented here explicitly:

$$\mu_c \equiv k_{cz}/a, \quad \mu_f \equiv k_{fz}/a, \quad \text{etc.} \qquad (7.5)$$

$$\lambda_b \equiv 2M(E_0 - E_b)/\hbar^2 a^2 , \qquad (7.6)$$

$$\lambda_c \equiv \mathrm{i} , \qquad (7.7)$$

$$A_{cc'} \equiv \frac{aL}{4(\mu_c \mu_{c'})^{\frac{1}{2}}} \frac{d^2}{D} V_{cc'} \quad \text{for } c \neq c' , \qquad (7.8)$$

$$A_{cb} \equiv \frac{(aL)^{\frac{1}{2}}}{2\mu_c^{\frac{1}{2}}} \frac{d^2}{D} V_{cb} , \qquad (7.9)$$

$$A_{bb'} \equiv \frac{d^2}{D} V_{bb'} \quad \text{for } b \neq b' , \qquad (7.10)$$

$$D_c \equiv \frac{aL}{4(\mu_0 \mu_c)^{\frac{1}{2}}} \frac{d^2}{D} t_{c0} , \qquad (7.11)$$

and

$$D_b \equiv \frac{\mathrm{i}(aL)^{\frac{1}{2}}}{2\lambda_b \mu_0^{\frac{1}{2}}} \frac{d^2}{D} t_{b0} . \qquad (7.12)$$

The final intensities have the same form as those (3.36):

$$R_f \equiv R_f(K_f, k_{fz}, v_f) = |\delta_{f,0} - 2\mathrm{i}\, D_f|^2 . \qquad (7.13)$$

The final quantum numbers are not arbitrary, but must satisfy the condition of energy conservation:

$$\hbar^2 (K_f^2 + k_{fz}^2) + 2ME_{\mathrm{vib}}(v_f) = \hbar^2 (K_0^2 + k_{0z}^2) + 2ME_{\mathrm{vib}}(v_0) . \qquad (7.14)$$

In the elastic treatment, the vibrational energy is unchanged and therefore disappears from (7.14). $K_f - K_0$ is equal to a reciprocal lattice vector, F, and (7.14) reduces to (2.10). The initial and final vibrational states of the solid are not observed in experiments to date; we must, therefore, average (7.13) over initial phonon states and sum over final phonon states.

As in section 3, an approximate, but unitary, t-matrix may be obtained by keeping only the imaginary part of $(E_0 - E_{g'} + \mathrm{i}\varepsilon)^{-1}$, that is $-\mathrm{i}\pi\delta(E_0 - E_{g'})$, in the integral over continuum states in (7.4); in this way, the following analogue of (3.25) is obtained for all g:

$$\mathrm{i}\lambda_g D_g = -A_{g0}(1 - \delta_{g,0}) + \mathrm{i} \sum_{g' \neq g} A_{gg'} D_{g'} , \qquad (7.15)$$

where we recall the definition (7.7).

In the case of elastic scattering, where the parallel momentum of the gas atom may change only by discrete amounts, the solution of (7.15) is straightforward, and some solutions are discussed in section 4. The case of inelastic scattering is more difficult since both the energy and momentum of the gas atom may change continuously over wide ranges of values. However, if we are willing to make the restriction that the gas atom exchanges only a single phonon with the solid, the solution of (7.15) is again straightforward. For example, if we consider a system with no diffraction and only "one-phonon beams", p, scattered around the specular beam, 0, the (unitary) dimensionless t-matrix, D_g, is given by the following set of equations:

$$D_0 = -\,\mathrm{i} \sum_p A_{0p} D_p , \tag{7.16a}$$

and

$$D_p = A_{p0}(1 - \mathrm{i}D_0), \tag{7.16b}$$

where $\sum_p$ implies summations over both K_p and v_p, and where v_p differs from v_0 only by the emission or absorption of a single phonon. From (7.13) and (7.16) it follows that the intensities are given by

$$R_0 = 1 - \sum_p R_p , \tag{7.17a}$$

and

$$R_p = \frac{4\,|A_{p0}|^2}{(1 + \sum_{p'} |A_{p'0}|^2)^2} . \tag{7.17b}$$

As a less trivial example, let us consider a system in which, in addition to undergoing inelastic processes, a gas atom may be diffracted into a bound state, b. With the one-phonon approximation, we obtain from (7.15)

$$\mathrm{i}D_0 = A_{0b} D_b + \sum_p A_{0p} D_p , \tag{7.18a}$$

$$-\,\mathrm{i}\lambda_b D_b = A_{b0}(1 - \mathrm{i}D_0) - \mathrm{i} \sum_p A_{bp} D_p , \tag{7.18b}$$

and

$$D_p = A_{p0}(1 - \mathrm{i}D_0) - \mathrm{i}A_{pb} D_b . \tag{7.18c}$$

The intensities, R_p, are found as usual by solving (7.18) for the D_p and substituting into (7.13).

These intensities, as well as those (7.17), must still be averaged over initial phonon states and summed over final phonon states; this has not yet been done. A reasonable approximation, which preserves unitarity, is to average separately each term in the numerators and denominators of the resulting expressions for the D_p. Then, diffraction matrix elements such as A_{b0} become matrix elements of the thermally-averaged potential defined by (2.1), re the parallel momentum of the gas ints, the solution of (7.15) is straight- sed in section 4. The case of inelastic e energy and momentum of the gas de ranges of values. However, if we he gas atom exchanges only a single (7.15) is again straightforward. For o diffraction and only "one-phonon r beam, 0, the (unitary) dimension- ing set of equations:

$A_{0p}D_p,$ (7.16a)

$- iD_0),$ (7.16b)

K_p and v_p, and where v_p differs from a single phonon. From (7.13) and given by

$R_p,$ (7.17a)

$\frac{\quad{}_0|^2}{A_{p'0}|^2)^2}.$ (7.17b)

der a system in which, in addition tom may be diffracted into a bound ation, we obtain from (7.15)

$A_{0p}D_p,$ (7.18a)

$)_0) - i \sum_p A_{bp}D_p.$ (7.18b)

$) - iA_{pb}D_b.$ (7.18c)

by solving (7.18) for the D_p and

), must still be averaged over initial honon states; this has not yet been ch preserves unitarity, is to average and denominators of the resulting n matrix elements such as A_{b0} be- veraged potential defined by (2.1),

while averages of summations such as $\sum_p |A_{p0}|^2$ may be found using methods developed by Van Hove[21]). These averaging problems are not discussed further in this paper.

In order to obtain a simple qualitative picture of the effects of a bound state resonance on inelastic scattering, and in particular on the specular intensity, let us simplify (7.18) by assuming that, near the resonance, phonon exchange is important only when the gas atom is already in the bound state. With this simplification in mind, we set $A_{0p} = A_{p0} = 0$ in (7.18) and derive from (7.13) that

$$R_0 = 1 - \sum_p R_p, \tag{7.19a}$$

and

$$R_p = \frac{4\,|A_{pb}A_{b0}|^2}{\lambda_b^2 + (|A_{b0}|^2 + \sum_{p'} |A_{p'b}|^2)^2}. \tag{7.19b}$$

Assuming that the matrix elements are sufficiently slowly-varying around the resonance, we obtain the important qualitative result that R_0 has a *minimum* and each R_p a maximum at exact resonance, when $\lambda_b = 0$. This result should be contrasted with the corresponding results for elastic scattering in sections 3 and 4, in which R_0 has a *maximum* ($R_0 = 1$) at exact resonance. That the experimentally-observed minimum in R_0 at resonance[19, 18]), discussed in section 6.2, is a result of inelastic, rather than of elastic, scattering was suggested by Lennard-Jones and Devonshire[22]).

Acknowledgments

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Appendix A. Evaluation of S_1 in (3.9)

In the limit of $L \to \infty$, (3.9) may be written as an integral:

$$S_1(z \to \infty) = \frac{L^{\frac{1}{2}}}{2\pi} \int_0^\infty \frac{(G\, q\, |t|\, 0\, k_z)}{(k_{Gz}^2 - q^2 + i\varepsilon)} \left[e^{i(qz + \zeta_q)} + e^{-i(qz + \zeta_q)} \right] dq\,, \tag{A1}$$

where we have taken the limit as $z \to \infty$ and substituted for ϕ_q from (2.16b). The contours chosen for evaluation of these integrals are shown in fig. A1. Contour A is chosen for the first integral, and contour B for the second.

Then, for a very general t-matrix [that is, for a very general $v(r)$], the contributions to the integrals from those parts of the contours which do not lie on the real axis vanish in the limit of $z \to \infty$. For this to be rigorously true, it is sufficient that the t-matrix has no singularities on the positive real axis;

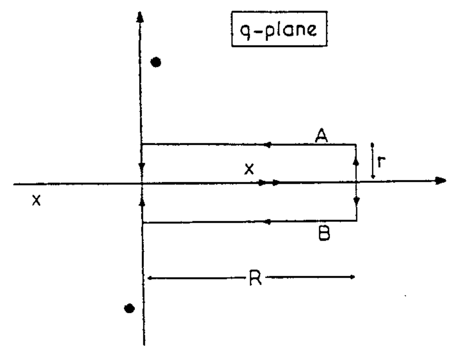


Fig. A1. Contours chosen for the integrals in (A1). The limits are $R \to \infty$ and $r > \varepsilon/2k_{Gz} \to 0$. (● poles for $k^2_{Gz} < 0$; × poles for $k_{Gz} > 0$).

this will be so for a physically realistic $v(r)$. The only contribution to the integrals, then, comes from the pole at $q = (k^2_{Gz} + i\varepsilon)^{\frac{1}{2}}$ when $k^2_{Gz} \geqslant 0$, and the result (3.10) is obtained.

Appendix B. Evaluation of S_2 (3.23)

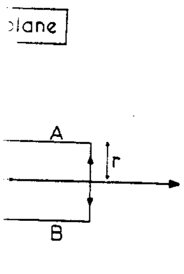
In the limit of $L \to \infty$, (3.23) may be written as an integral:

$$S_2 = \frac{L}{2\pi} \int_0^\infty \frac{(\alpha | v_{G-G'} | q)(G' \, q | t | \mathbf{0} \, k_z)}{(k^2_{G'z} - q^2 + i\varepsilon)} \, dq \,, \tag{B1}$$

and the contour chosen for its evaluation is shown in fig. B1. It is assumed that the integral is equal to one-half of this contour integral, and that the only significant contribution to this contour integral is from the pole at $q = (k^2_{G'z} + i\varepsilon)^{\frac{1}{2}}$ when $k^2_{G'z} \geqslant 0$. The result (3.24) follows.

That this is only an approximation is clear, for example, from the fact that the contribution when $k^2_{G'z} < 0$ is ignored; this is equivalent to ignoring the beams which are "diffracted into the surface". The approximation is more serious, however, as singularities of both $(\alpha | v_{G-G'} | q)$ and $(G' \, q | t | \mathbf{0} \, k_z)$ in the upper half of the q-plane are ignored also.

for a very general $v(r)$], the contri- of the contours which do not lie ∞. For this to be rigorously true, gularities on the positive real axis;



in (A1). The limits are $R \to \infty$ and 0: $\times$ poles for $k_{Gz} > 0$).

r). The only contribution to the $= (k_{Gz}^2 + i\varepsilon)^{\frac{1}{2}}$ when $k_{Gz}^2 \geqslant 0$, and the

on of S_2 (3.23)

ritten as an integral:

$$G' \, q \,|t|\, 0 \, k_z) \over q^2 + i\varepsilon) \, dq \,, \qquad \text{(B1)}$$

is shown in fig. B1. It is assumed this contour integral, and that the ntour integral is from the pole at 3.24) follows.

ear, for example, from the fact that : this is equivalent to ignoring the face". The approximation is more $(\alpha|v_{G-G'}|\,q)$ and $(G' \, q\,|t|\, 0 \, k_z)$ in also.

The contributions when $k_{G'z}^2 < 0$ could easily be included in the above formalism; for simplicity, however, they are not considered further in this paper.

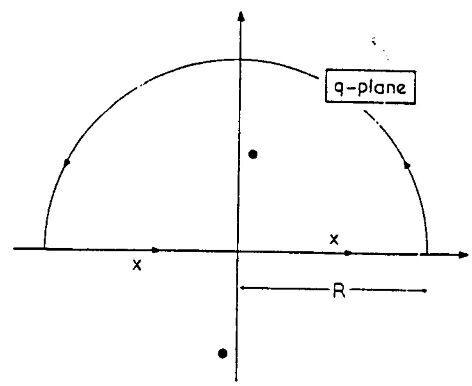


Fig. B1. Contour chosen for the integral in (B1). The limit is $R \to \infty$. ($\bullet$ poles for $k^2{}_{G'z} < 0$; $\times$ poles for $k^2{}_{G'z} > 0$).

Appendix C. Proof of unitarity (3.38)

In this appendix we use: (i) the convention of summation over repeated indices α and β and (ii) the convention that summations over F, G and G' do *not* include the zero reciprocal lattice vector.

Then, from (3.33), (3.36) and (3.38), we observe that we are required to prove that

$$2Z \equiv |1 - 2 \sum_G A_{0\alpha}^{0G} D_G^\alpha|^2 - 1 + 4 \sum_F |D_F^F|^2 = 0 \,. \qquad \text{(C1)}$$

We have

$$Z = - \sum_G (D_G^{\alpha *} A_{\alpha 0}^{G0} + A_{0\alpha}^{0G} D_G^\alpha) + 2 \sum_{G,\,G'} D_{G'}^{\beta *} A_{\beta 0}^{G'0} A_{0\alpha}^{0G} D_G^\alpha + 2 \sum_F |D_F^F|^2 \,. \qquad \text{(C2)}$$

It follows from (3.28) and (3.29) that we may define an X_α^G such that

$$\begin{aligned} X_\alpha^G = \sum_{G'} A_{\alpha 0}^{G0} A_{0\beta}^{0G'} D_{G'}^\beta + i \sum_{G,\,G' \neq G} A_{\alpha\beta}^{GG'} D_{G'}^\beta + i A_{\alpha\beta}^{GG} D_G^\beta \\ + i \sum_{m,\,G'} A_{\alpha m}^{G0} A_{m\beta}^{0G'} D_{G'}^\beta / \lambda_m^0 - A_{\alpha 0}^{G0} = 0 \,. \end{aligned} \qquad \text{(C3)}$$

Therefore,

$$\begin{aligned} 0 &= \sum_G (X_\alpha^G D_G^{\alpha *} + X_\alpha^{G*} D_G^\alpha) \\ &= \sum_{G,\,G'} (D_G^{\alpha *} A_{\alpha 0}^{G0} A_{0\beta}^{0G'} D_{G'}^\beta + D_{G'}^{\beta *} A_{\beta 0}^{G'0} A_{0\alpha}^{0G} D_G^\alpha) \end{aligned}$$

$$+ \mathrm{i} \sum_{G, G' \neq G} (D_G^{\alpha *} A_{\alpha\beta}^{GG'} D_{G'}^{\beta} - D_{G'}^{\beta *} A_{\beta\alpha}^{G'G} D_G^{\alpha})$$
$$+ \mathrm{i} \sum_G (D_G^{\alpha *} A_{\alpha\beta}^{GG} D_G^{\beta} - D_G^{\beta *} A_{\beta\alpha}^{GG *} D_G^{\alpha})$$
$$+ \mathrm{i} \sum_{m, G, G'} (D_G^{\alpha *} A_{\alpha m}^{G0} A_{m\beta}^{0G'} D_{G'}^{\beta} - D_{G'}^{\beta *} A_{\beta m}^{G'0} A_{m\alpha}^{0G} D_G^{\alpha})/\lambda_m^0$$
$$- \sum_G (D_G^{\alpha *} A_{\alpha 0}^{G0} + A_{0\alpha}^{0G} D_G^{\alpha}). \tag{C4}$$

The two terms in the first summand are equal; the two pairs of terms in the second and fourth summands cancel; on account of (3.26) and (3.30), the only terms remaining in the third summand are those for which *both* $\alpha=\beta$ *and* $G=F$, when the two terms in the summand are equal. We are left with

$$0 = 2 \sum_{G, G'} D_G^{\alpha *} A_{\alpha 0}^{G0} A_{0\beta}^{0G'} D_{G'}^{\beta} + 2 \sum_F |D_F{}^F|^2$$
$$- \sum_G (D_G^{\alpha *} A_{\alpha 0}^{G0} + A_{0\alpha}^{0G} D_G^{\alpha}) = Z, \tag{C5}$$

which completes the proof.

References

1) J. B. Anderson, R. P. Andres and J. B. Fenn, in: *Advances in Atomic and Molecular Physics*, Vol. 1 (Academic Press, New York, 1965) p. 345.
2) J. P. Moran, M.I.T. Fluid Dynamics Research Laboratory Report T 68-1 (Feb. 1968).
3) D. R. O'Keefe, U.T.I.A.S. Report No. 132 (July 1968).
4) S. S. Fisher, M. N. Bishara, A. R. Kuhlthau and J. E. Scott, Jr., in: *Rarefied Gas Dynamics*, Suppl. 5, Vol. 2 (Academic Press, New York, 1969) p. 1227.
5) N. Cabrera, V. Celli and R. Manson, Phys. Rev. Letters **22** (1969) 346.
6) L. Trilling, in: *Fundamentals of Gas-Surface Interactions* (Academic Press, New York, 1967) p. 392.
7) R. E. Stickney, in: *Advances in Atomic and Molecular Physics*, Vol. 3 (Academic Press, New York, 1967) p. 143.
8) F. O. Goodman, J. Chem. Phys. **50** (1969) 3855.
9) R. M. Logan, Surface Sci. **15** (1969) 387.
10) E. C. Beder, ref. 7, p. 205.
11) P. Feuer and C. Osburn, ref. 4, p. 1095.
12) See the references given on pp. 288 and 289 of ref. 10.
13) See, for example, T. Y. Wu and T. Ohmura, *Quantum Theory of Scattering* (Prentice-Hall, Englewood Cliffs, N.J., 1962).
14) P. Morse, Phys. Rev. **34** (1929) 57.
15) R. J. Glauber, Phys. Rev. **98** (1955) 1692.
16) C. Strachan, Proc. Roy. Soc. (London) A **150** (1935) 456.
17) J. E. Lennard-Jones and C. Strachan, Proc. Roy. Soc. (London) A **150** (1935) 442.
18) R. Frish and O. Stern, Z. Physik **84** (1933) 430.
19) J. E. Lennard-Jones and A. F. Devonshire, Nature **137** (1936) 1069.
20) E. G. McRae, J. Chem. Phys. **45** (1966) 3258.
21) L. Van Hove, Phys. Rev. **95** (1954) 249.
22) J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. (London) A **158** (1937) 253.